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10APR03 E799103-1 D02246
P01/7700 0.00-0308215.3

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Ceres Power Limited
Unit 18, Denvale Trade Park
Haslett Avenue East
Crawley, United Kingdom RH10 1SS

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom 8243818002

4. Title of the invention

Densification of Ceria Based Electrolytes

5. Name of your agent *(if you have one)*

D Young & Co

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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D Young & Co (Agents for the Applicants)

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Densification of Ceria Based Electrolytes

The present invention relates to the densification of ceria based electrolytes as may be used in fuel cells and oxygen generators for example.

Procedures are known for fabricating thick film solid oxide fuel cell (SOFC) structures onto porous ferritic stainless steel foil substrates. The metal supported single cells can then easily be assembled into arrays by laser welding the individual cells onto a metal bi-polar plate. Such technology is described in GB 2,368,450. It has also been demonstrated that ceria based electrolytes, eg $Ce_{0.9}Gd_{0.1}O_{1.95}$(CG10) could be sintered on a metallic substrate to provide a dense impermeable electrolyte film at lower temperatures than previously used. The ability to sinter electrolytes at lower temperatures, eg 1000°C minimises degradative changes to the stainless steel microstructure, reduces fabrication costs and also reduces the concentration of transition metal cations in the electrolyte due to transport of gaseous metal species from the substrate and its protective oxide.

EP-A-1000913 describes processes for producing dense (>97% of the theoretically achievable density) ceria electrolytes at relatively low temperatures (~1000°C). This patent application demonstrates that when small amounts (1-2mol%) of CuO, NiO or CoO are added to commercial ceria based electrolyte powders (eg supplied by Rhodia, France) then pellets pressed from these doped pellets can be sintered to densities greater than 97% of the theoretical achievable density at temperatures as low as 1000°C compared to 1350°C usually required for pellets without any transition metal cation additions. It should be noted that at densities of 97% of the theoretical achievable density the ceria based electrolytes are impermeable and so significantly reduce gaseous leakage between the anode and cathode gases.

However the addition of transition metal cations is not without problems. EMF measurements have been carried out at 650°C on thin (~1mm) discs fabricated from the sintered powders. EMF values (910mV) for electrolyte discs without additions of divalent cations were at least 100m V higher than values recorded (800mV) for thin discs containing 2 mole % Co^{2+} or 1 mole % Mn^{2+} using similar experimental conditions. Clearly additions of the transition metal cations has introduced significant electronic conductivity which is an undesirable side-effect as it would have a major

impact on the performance characteristics of intermediate-temperature solid oxide fuel cell (IT-SOFC) stacks incorporating ceria based electrolytes with cation additives.

~~It is an object of the present invention to assist in overcoming one or more of~~ the problems described above to enable the sintering of dense electrolytes without an excessive reduction in EMF.

According to a first aspect of the present invention there is provided a method of determining the effective concentration of divalent cations in a fabricated electrolyte, the method comprising

determining the concentration of divalent cations in a fabricated electrolyte;

determining the concentration of trivalent cations in a fabricated electrolyte and subtracting the adjusted concentration of trivalent cations from the concentration of divalent cations to produce the effective concentration of divalent cations. Due to the deleterious effect of the trivalent cations it is necessary to multiply their measured concentration by a factor between 5 and 10 as described later.

This method enables the effective concentration of divalent actions in an electrolyte to be determined. Once the effective concentration of divalent actions can be determined, it may be optimised to ensure sufficient densification of the electrolyte under desired conditions, eg approximately 1000°C. It should be emphasised that the procedures described herein apply to deposited 'green' electrolyte layers having typical densities in the range 50-60%. Fabrication routes capable of attaining this requirement have been described in patent application GB 0205291, and a preferred method involves depositing the electrolyte powder by EPD followed by isostatic pressing.

Both divalent and trivalent cations can be incorporated into an electrolyte film during the fabrication procedures, but it has been found that their roles are very different. Divalent cations can enhance the densification process whereas it has been found that the presence of trivalent cations have an adverse effect on the densification process. To ensure electrolyte densification at 1000°C it has been found that the concentration of divalent cations should exceed the concentration of trivalent cations, and it can be necessary to deliberately add small quantities of divalent cations (eg Mn^{2+}, Fe^{2+}, Mg^{2+}, etc) to overcome the deleterious effects of trivalent cations (eg Cr^{3+}, Fe^{3+}, Al^{3+}, etc) in the electrolyte.

The concentration of divalent cations in a fabricated electrolyte may be determined by adding the concentration of divalent cations that were added to the electrolyte prior to completion of the fabrication process to the concentration of divalent cations determined to be in the electrolyte after the fabrication process, had there been no additions.

Divalent cations present in the electrolyte after the fabrication process could have originated from a number of sources. Divalent cations can originate from the conversion or reduction of intrinsic trivalent cations into divalent cations. For example the processing conditions during the fabrication procedure can be modified to reduce the concentration of deleterious trivalent cations, for example Fe^{3+} can be reduced to Fe^{2+} by appropriate control of the oxygen or water partial pressure in a sintering furnace. Divalent cations in the electrolyte could have originated from vapours from a metal substrate and/or an oxide layer on a metal substrate. Divalent cations can be added to the electrolyte at an appropriate opportunity, eg prior to the sintering process. The magnitude and type of the various cation impurity levels in turn influence the sintering kinetics and determine whether adequate densification of the electrolyte (generally required to be greater than 97% of the achievable density for desirable results) can be achieved by 1000°C.

The inventors of the present invention have surprisingly found that an effective concentration of divalent cations (concentration of divalent cations – adjusted concentration of trivalent cations) of between 0.01 mole % and 0.1 mole % inclusive can be used to produce an electrolyte with a density greater than 97% of the achievable density at approximately 1000°C. Furthermore such an effective concentration of divalent cations does not produce as severe a reduction in EMF as electrolytes containing greater concentrations of divalent cations.

Preferably the effective concentration of divalent cations is between 0.02 mole % and 0.09 mole % inclusive.

More preferably the effective concentration of divalent cations is between 0.03 mole % and 0.08 mole % inclusive.

According to a second aspect of the present invention there is provided a method of preparing an electrolyte with a desired effective cation concentration, the

method comprising fabricating an electrolyte and before or during fabrication increasing the divalent cation concentration by one or more of the following:

receiving divalent cations from vapour produced by a metal substrate associated with the electrolyte or an oxide layer on the substrate;

reducing trivalent cations in the substrate material into divalent cations; or

specifically adding divalent cations to the electrolyte prior to or during fabrication;

such that the effective concentration of divalent cations minus the adjusted concentration of trivalent cations in the fabricated electrolyte is within a desired range.

The desired range may include or be between 0.01% and 0.1 mole %, but is preferably between 0.02 mole % and 0.09 mole % inclusive and more preferably between 0.03 mole % and 0.08 mole % inclusive.

According to a third aspect of the present invention there is provided an electrolyte with an effective concentration of divalent cations determined by subtracting an adjusted concentration of trivalent cations in the electrolyte from the concentration of divalent cations in the substrate. The effective cation concentration may be between 0.01 mole % and 0.1 mole % inclusive, but is preferably between 0.02 mole % and 0.09 mole % inclusive and is more preferably between 0.03 mole % and 0.08 mole % inclusive.

According to a fourth aspect of the present invention there is provided a half cell comprising a substrate, an electrode and an electrolyte according to the third aspect of the present invention.

According to a fifth aspect of the present invention there is provided a fuel cell comprising the half cell of the fourth aspect of the present invention provided with a further electrode on the opposite side of the electrolyte from the other electrode.

According to an sixth aspect of the present invention there is provided an oxygen generator comprising the half cell of the fourth aspect with a further electrode on the opposite side of the electrolyte from the other electrode.

Preferred embodiments of the present invention will now be described herein below by way of example only with reference to the accompanying drawings, in which:

Figure 1 illustrates the sintering characteristics of ceria based electrolyte pellets for 0, 1% and 2% addition of cations;

Figure 2 illustrates the sintering characteristics of ceria based electrolyte pellets for 0 and 0.1% addition of cations and

Figure 3 is a schematic representation of a metal foil supported thick film cell assembly.

Experiments have been carried out using a titanium-niobium stabilised ferritic stainless steel substrate (~ 18% Cr) with the designation 1.4509. Analysis of a sintered electrolyte on the substrate indicated cation impurity levels of Fe^{2+} (0.25 mole %) and Cr^{3+} (0.005 mole %). Subsequent investigations have shown that densification of the CGO10 electrolyte can be accomplished using a variety of ferritic stainless steels with different initial compositions and oxidation characteristics. These different substrates together with processing variations can produce significant changes in the concentration and valence of the metal impurities incorporated into the CGO electrolyte.

Studies on the sintering characteristics of a ceria based electrolyte, $Ce_{0.9}Gd_{0.1}O_{1.95}$, powder are summarised in Fig 1. Inspection of Fig 1 reveals that 1-2 mole % cation additions of divalent cations (eg Co^{2+}, Fe^{2+}, Mn^{2+}) can produce technologically useful pellet densities around 97/98% of the theoretical achievable density, whereas the trivalent cations (Fe^{3+}, Mn^{3+}) severely retard the sintering kinetics. Fig 2 shows that for cation additions at the 0.1% levels the density of fired pellets was about the same for each of the additions of Mn^{2+}, Mg^{2+}, Ca^{2+}, and comparable to densities (~93% of the theoretical achievable density) developed by the pellets without cation additions as mentioned earlier. Co^{2+} and Fe^{2+} reduced the sintering kinetics, and particularly noteworthy is the very large decrease in sintered density due to additions of Fe^{3+} and Cr^{3+}, even for cation additions as low as 0.1%.

The studies summarised in Figs 1 and 2 show that the addition of divalent cations enhances the densification process, whereas the presence of trivalent cations has an adverse effect on the densification process. However, these studies indicate that ceria based pellets require a divalent cation concentration of the order of 2% to produce densification of 97% of the theoretical achievable density. The studies

summarised in Figs 1 and 2 highlight how surprising it is that dense electrolyte thick films can be produced with apparently lower divalent cation concentrations.

The observed densification of the electrolyte thick films compared to pellets could be associated with the realisation that the sintering process is taking place within an oxygen partial pressure gradient. The associated oxygen flux contributes to oxidation of the metal substrate foil. At the same time a small but significant cation flux in the opposite direction influences the sintering kinetics which are controlled by cation transport as illustrated in Fig 3. Both anionic and cation fluxes can be produced when multi-component oxide phases are placed in oxygen chemical potential gradients, and the associated differential transport processes can be responsible for de-mixing phenomena. Whatever the details of the enhanced sintering mechanism its manifestation is an important technological innovation, and investigations by the applicants have provided information related to optimisation of the processing parameters to densify ceria electrolytes which may be used in SOFC structures supported on metal substrates, oxygen generators etc.

The following empirical equation has been developed to ensure high (> 98% of the theoretical achievable density) electrolyte densities, and to optimise the processing conditions for a variety of metal substrates, anode compositions, and SOFC configurations.

$$\lfloor M_E^{2+} \rfloor = \lfloor M_A^{2+} \rfloor + \lfloor M_I^{2+} \rfloor - Y \lfloor M_I^{3+} \rfloor \ldots\ldots\ldots\ldots\ldots\ldots (A)$$

$\lfloor M_E^{2+} \rfloor$ represents the effective concentration of divalent cations (eg Mn^{2+}, Fe^{2+}, Mg^{2+}, etc) in a specific electroylte. Experiments suggest that minimum effective concentrations of divalent cations required to ensure densification (> 98% of the theoretical achievable density) are typically 0.01-0.1 mole % (200-1000ppm), which are below values mentioned in earlier publications such as EP-A-1000913. It should be noted that the valence of selected cation impurities, e.g. Fe, Mn, will depend upon the oxygen partial pressure established within the sintering furnace.

$[M_A^{2+}]$ represents the concentration of divalent cations (eg, Mn^{2+}, Fe^{2+}, Mg^{2+}, etc) that were added to electrolyte prior to the high temperature fabrication procedures.

$[M_I^{2+}]$ represents the concentration of divalent cations (eg Mn^{2+}, Fe^{2+}, etc) determined to be in the electrolyte after the fabrication processes (without prior additions). The concentration of impurities can be determined by dynamic SIMS or Glow Discharge Optical Emission Spectrography (GDOES). Divalent cations are beneficial for enhanced sintering at 1000°C.

NOTE: ideally $|M_I^{2+}|$ should not exceed 0.1% for Fe^{2+} and Mn^{2+} ions, to avoid significant electronic conductivity in the electrolyte

The divalent cations in the electrolyte after the fabrication process could have originated from vapours from the metal substrate, or oxide on the substrate or from reduction of trivalent cations in the electrolyte layer for example.

$[M_I^{3+}]$ represents the concentration of trivalent cations (eg Fe^{3+}, Cr^{3+}, Al^{3+}, etc) determined to be in the electrolyte after the fabrication processes. The concentration of impurities is determined as above for the determination of the concentration of divalent cations in the electrolyte after the fabrication processes without prior additions. Trivalent cations are deleterious for sintering enhancement at 1000°C.

Y represents a multiplying factor (typically 5-10). The presence of trivalent cations is very deleterious for the sintering process and so their actual concentration has to be multiplied by the factor Y to take account of their severe impact on the sintering behaviour. It can also be necessary to vary the value of Y according to the nature and distribution of the trivalent cations. For example, the influence of Al^{3+} in discrete Al_2O_3 particles introduced during milling processes, differs from the role of Al^{3+} interfacial species widely distributed over the surface of the CGO powder.

Examples

Fig 3 shows a schematic representation of a metal foil supported thick film cell assembly as used in some of the following examples.

1. CGO is deposited directly onto 1.4509 metal substrate (no pre-oxidation Treatment). The CGO is sintered at 1000°C in a H_2/H_2O/argon atmosphere designed to establish a pO_2 value of 10^{-14} at 1000°C. $[M_E^{2+}]$ was determined to be +0.1% (Table 1) and dense electrolyte was produced. The Fe and Cr are transported into the electrolyte via the vapour phase species, eg: Fe(g), $Fe(OH)_2$ (g), Cr(g), $Cr(OH)_3$ (g). Note the concentration of gaseous metal hydroxide species will be influenced by metal thermodynamic activity in the metal oxide coating, and the p (H_2O) in sintering furnace (processing variable).

2. A CGO electrolyte film is deposited directly onto 1.4509 metal substrate (pre-oxidation treatment) and sintered at 1000°C in CO_2/H_2 argon atmosphere designed to establish pO_2 value of 10^{-14} at 1000°C. $[M_E^{2+}]$ was found to be – 0.07% (Table 1) due to Al^{3+} contamination. The electrolyte was not dense.

3. A Ni-CGO anode is fabricated on top of a 1.4509 metal substrate (pre-oxidation treatment). A CGO film is next deposited on top of the anode (see Fig 3), and sintered at 1000°C in a CO_2/H_2/argon atmosphere designed to establish pO_2 value of 10^{-14} at 1000°C. $[M_E^{2+}]$ was found to be –0.05% (Table 1) due to Al^{3+} contamination. The electrolyte was not dense.

4. A Ni-CGO anode is fabricated on top of a JS-3 metal substrate (pre-oxidation treatment). A CGO film is next deposited on top of the anode (see Fig 3), and sintered at 1000°C in a H_2/H_2O/argon atmosphere designed to establish pO_2 value of 10^{-14} at 1000°C. $[M_E^{2+}]$ was found to be +0.1% (Table 1) due to high Mn^{3+} content in spite of Al^{3+} contamination.

A dense electrolyte was produced.

5. A Ni-CGO anode is fabricated on top of a JS-3 metal substrate (pre-oxidation treatment). Mn (0.1cation%) was added to the CGO powder. A CGO film is next deposited on top of the anode (see Fig 3), and sintered at 1000°C in a H_2/H_2O/argon atmosphere designed to establish pO_2 value of 10^{-14} at 1000°C. $\left[M_E^{2+}\right]$ was found to be +0.1% (Table 1) due to high Mn^{3+} content in spite of Al^{3+} contamination and Fe present as Fe^{3+}.

A dense electrolyte was produced.

6. A Ni-CGO anode is fabricated on top of a ZMG 232 metal substrate (pre-oxidation treatment). A CGO film is next deposited on top of the anode (see Fig 3), and sintered at 1000°C in a H_2/H_2O/argon atmosphere designed to establish pO_2 value of 10^{-14} at 1000°C. $\left[M_E^{2+}\right]$ was found to be +0.08% (Table 1) due to high Mn^{3+} content in spite of Al^{3+} contamination.

A dense electrolyte was produced.

Table 1

Ferritic Stainless Steel Substrate	**Oxide**	**Anode**	**Electrolyte**				**Result**
			$\left[M_A^{2+}\right]$ %	$\left[M_I^{2+}\right]$ %	Y $\left[M_I^{3+}\right]$ %	$\left[M_E^{2+}\right]$ %	
1.4509	NT	NP	0	0.15	0.05	+ 0.1	Dense
1.4509	T	NP	0	0.03	0.1	- 0.07	Not dense
1.4509	T	Ni-CGO	0	0.05	0.1	- 0.05	Not dense
JS-3	T	Ni-CGO	0	0.2	0.1	+0.1	Dense
JS-3	T	Ni-CGO	0.1	0.1	0.1	+0.1	Dense
ZMG 232	T	Ni-CGO	0	0.2	0.12	+0.08	Dense

NT indicates no pre-treatment to form oxide layer

Presence of Ni-CGO reduces concentration of Cr and Fe in electrolyte (these species probably trapped as $NiFe_2O_4$, $NiCr_2O_4$). Unless there is sufficient divalent cations such as Mn^{2+} (eg JS-3) then the electrolyte is not dense.

CLAIMS

1. A method of determining the effective concentration of divalent cations in a fabricated electrolyte, the method comprising

determining the concentration of divalent cations in a fabricated electrolyte;

determining the concentration of trivalent cations in a fabricated electrolyte and subtracting the adjusted concentration of trivalent cations from the concentration of divalent cations to produce the effective concentration of divalent cations.

2. A method according to claim 1, wherein the concentration of divalent cations in a fabricated electrolyte is determined by adding the concentration of divalent cations that were added to the electrolyte prior to completion of a fabrication process to the concentration of divalent cations determined to be in the electrolyte after the fabrication process, had there been no additions.

3. A method according to claim 1 or claim 2, wherein at least some of the divalent cations are produced in the electrolyte by converting or reducing trivalent cations into divalent cations.

4. A method according to claim 3, wherein trivalent cations are converted or reduced into divalent cations during the fabrication process.

5. A method according to claim 4, wherein trivalent cations are converted or reduced into divalent cations during the fabrication process by appropriate control of an oxygen or water partial pressure in a sintering furnace.

6. A method according to any one of the preceding claims, wherein divalent cations are added to the electrolyte prior to completion of the fabrication process.

7. A method according to any one of the preceding claims, wherein at least some of the divalent cations in the electrolyte originate from vapours produced from a metal substrate or an oxide layer on a metal substrate.

8. A method according to any one of the preceding claims, wherein the concentration of cations is controlled such that the effective concentration of divalent cations is arranged to be between 0.01 mole % and 0.1 mole % inclusive.

9. A method according to claim 8, wherein the effective concentration of divalent cations is arranged to be between 0.02 mole % and 0.09 mole % inclusive.

10. A method according to claim 9, wherein the effective concentration of divalent cations is arranged to be between 0.03 mole % and 0.08 mole % inclusive.

11. A method according to any one of the preceding claims, wherein the determined concentration of trivalent cations is adjusted by multiplication typically by a factor between 5 and 10.

12. A method of preparing a ceria based electrolyte with a density greater than 97% of the theoretical achievable density, the method comprising;

providing a ceria based electrolyte and

sintering the electrolyte at 1200°C or less such that the concentration of divalent cations minus the adjusted concentration of trivalent cations in the sintered electrolyte is between 0.01 mole % and 0.1 mole %.

13. A method according to claim 12, wherein the conditions of the sintering process are controlled to reduce at least some trivalent cations in the electrolyte into divalent cations.

14. A method according to claim 13, wherein the conditions of the sintering process are controlled to produce a suitable oxygen or water pressure to reduce a suitable amount of trivalent cations into divalent cations.

15. A method according to claim 12, claim 13 or claim 14, wherein the electrolyte

is provided on a substrate and the substrate material is selected to produce the required concentration of divalent cations minus the adjusted concentration of trivalent cations in the electrolyte.

16. A method according to claim 15, wherein an electrode is provided between the electrolyte and the substrate.

17. A method according to any of claims 12 to 16, wherein divalent cations are added to the electrolyte before or during the sintering process.

18. A method according to any of claims 12 to 17, wherein the concentration of divalent cations minus the adjusted concentration of trivalent cations in the sintered electrolyte is between 0.02 mole % and 0.09 mole % inclusive.

19. A method according to claim 18, wherein the concentration of divalent cations minus the adjusted concentration of trivalent cations in the sintered electrolyte is between 0.03 mole % and 0.08 mole % inclusive.

20. A method according to any of claims 12 to 19, wherein the concentration of trivalent cations is adjusted by multiplication by a number between 5 and 10.

21. A method according to any claims 12 to 20, wherein the electrolyte is sintered at 1100°C or less.

22. A method according to claim 21, wherein the electrolyte is sintered at 1050°C or less.

23. A method according to claim 22, wherein the electrolyte is sintered at 1000°C or less.

24. A method according to any one of claims 12 to 23, wherein the electrolyte is provided as a thick film.

25. A ceria based electrolyte with a density greater than 97% of the theoretical achievable density and with a concentration of divalent cations minus an adjusted concentration of trivalent cations of between 0.01 mole % and 0.1 mole % inclusive.

26. An electrolyte according to claim 25, wherein the concentration of divalent cations minus an adjusted concentration of trivalent cations is between 0.02 mole % and 0.09 mole % inclusive.

27. An electrolyte according to claim 26, wherein the concentration of divalent cations minus an adjusted concentration of trivalent cations is between 0.03 mole % and 0.08 mole % inclusive.

28. An electrolyte according to any of claims 25 to 27, wherein the concentration of trivalent cations is adjusted by multiplication by a number between 5 and 10.

29. An electrolyte according to any claims 25 to 28, wherein the electrolyte is provided as a thick film.

30. A half cell assembly comprising a substrate, an electrode and an electrolyte according to any of claims 25 to 29.

31. A fuel cell assembly comprising a half cell according to claim 30 and a further electrode provided on the opposite side of the electrolyte from the first electrode.

32. A fuel cell according to claim 31, wherein the first electrode is an anode and the further electrode is a cathode.

33. An oxygen generator comprising a half cell assembly according to claim 30 and a further electrode provided on the opposite side of the electrolyte from the first electrode.

ABSTRACT

Densification of Ceria Based Electrolytes

The fabrication of ceria based electrolytes to densities greater than 97% of the theoretical achievable density at temperatures below 1200°C, preferably approximately 1000°C, is disclosed. The electrolyte has a concentration of divalent cations minus an adjusted concentration of trivalent cations of between 0.01 mole % and 0.1 mole %.

Fig 1

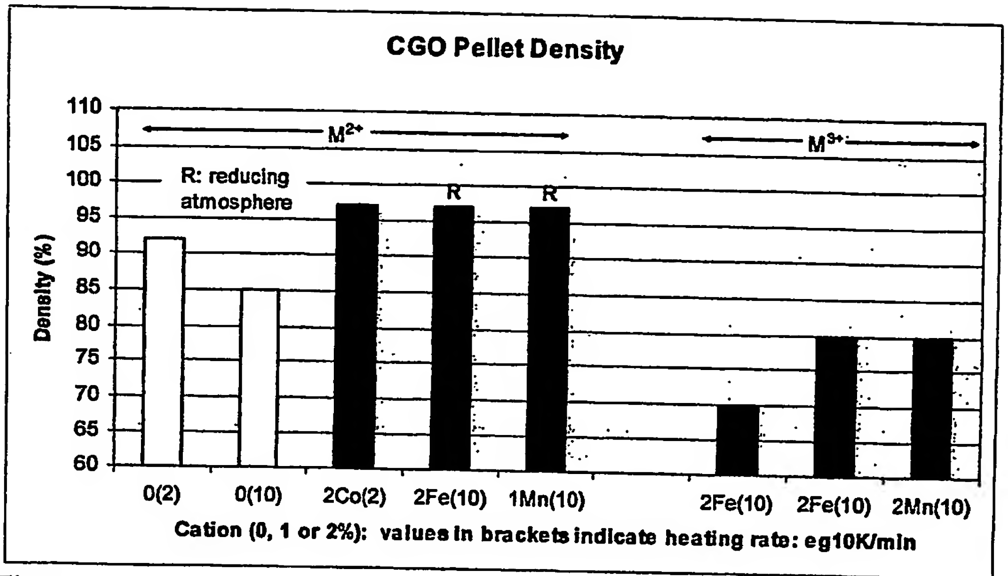

CGO Pellet Density
110
105
100
95
90
85
80
75
70
65
60
Density (%)
M2+
M3+
R: reducing atmosphere
R
R
0(2)
0(10)
2Co(2)
2Fe(10)
1Mn(10)
2Fe(10)
2Fe(10)
2Mn(10)
Cation (0, 1 or 2%): values in brackets indicate heating rate: eg10K/min

Fig 2

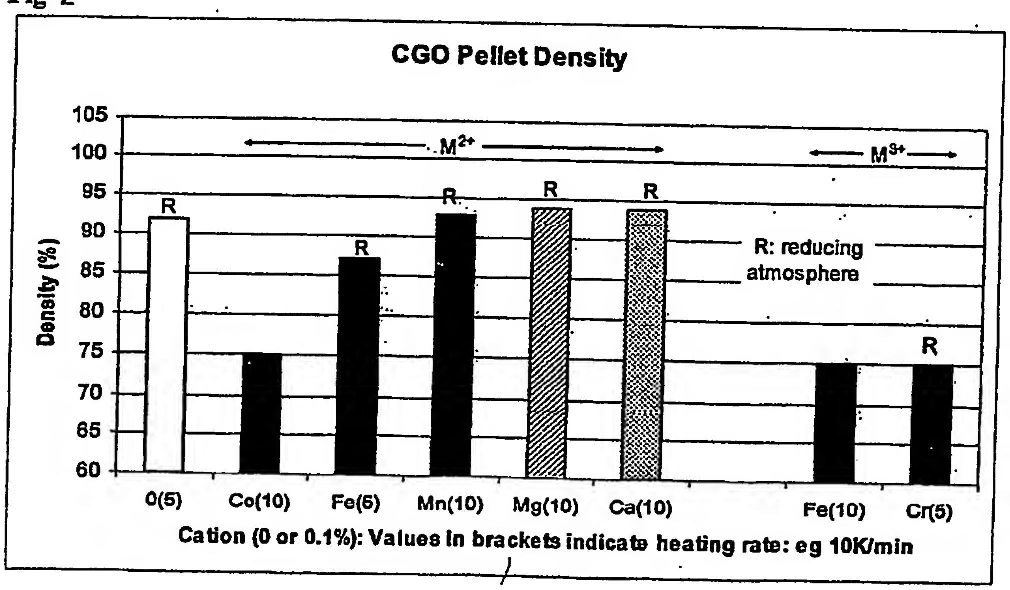
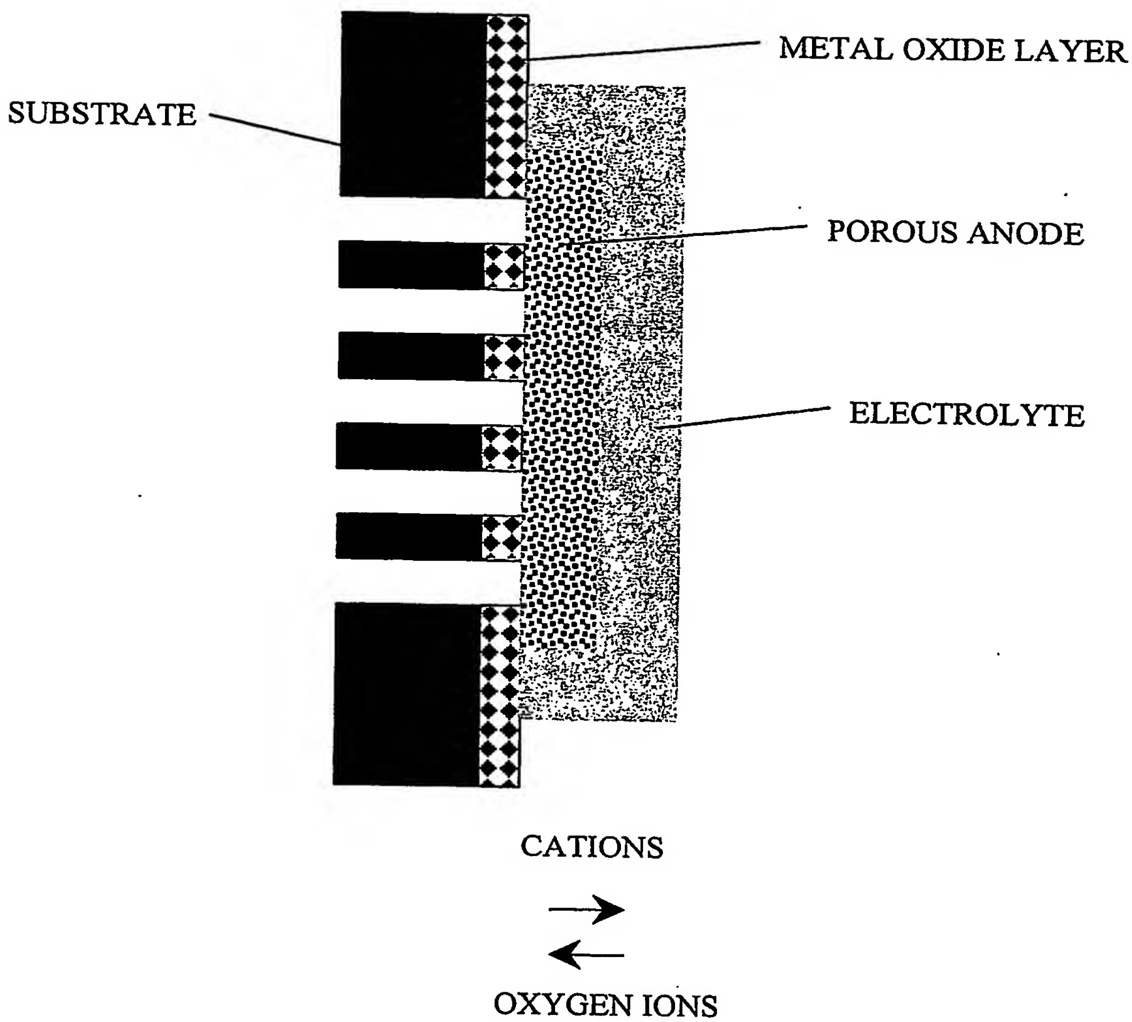

CGO Pellet Density
105
100
95
90
85
80
75
70
65
60
Density (%)
M2+
M3+
R: reducing atmosphere
R
R
R
R
R
R
0(5)
Co(10)
Fe(6)
Mn(10)
Mg(10)
Ca(10)
Fe(10)
Cr(5)
Cation (0 or 0.1%): Values in brackets indicate heating rate: eg 10K/min

Figure 3.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